"On the Refractive Indices and Densities of Normal and Seminormal Aqueous Solutions of Hydrogen Chloride and the Chlorides of the Alkalis." By Sir John Conroy, Bart., M.A., F.R.S., Fellow and Bedford Lecturer of Balliol College, and Millard Lecturer of Trinity College, Oxford. Received December 15, 1898,—Read January 19, 1899.

A very large number of observations have been made of the refractive indices and densities of aqueous solutions of inorganic salts and acids: in England, more especially, by Dr. J. H. Gladstone, who in a paper in the 'Philosophical Transactions' for 1870, gave the values he had obtained for the refractive indices and densities of some 160 salts and acids; and in a series of papers published subsequently in the 'Journal of the Chemical Society,' has given the results of further observations.

Most, however, of these determinations have been made with solutions of different strengths, and at different temperatures, and, therefore, I venture to bring before the Royal Society an account of some observations I have made of the refractive indices and densities of normal and semi-normal aqueous solutions of hydrogen chloride, and the chlorides of the alkalis at a uniform temperature of 18°.

The method was the ordinary hollow prism one, but special care was taken to keep the solution at a definite known temperature. An alteration of 1° in the temperature of water in the neighbourhood of 20° makes a difference in the refractive index of nearly one unit in the fourth decimal place.*

The goniometer used was made by Messrs. Troughton and Simms; it has an 8-inch circle divided into 10′, and is read by means of two micrometers, directly to 10″, and by estimation to single seconds. The prism was made by Steinheil; the value of its refracting angle, as determined by ten independent measurements, was 60° 1′ 44″. The prism table was supported independently of the divided circle by means of a steel axis.

In order that the temperature of the prism might be kept constant, it was surrounded by a water-jacket, the prism being in actual contact with the metal casing containing the water, as, in some previous experiments,† it had been found that when the prism was merely surrounded by the water-jacket, without being in actual contact with it, a considerable time elapsed before the prism and water-jacket were

^{*} Conf. Landolt and Börnstein's 'Tables,' p. 419.

^{† &}quot;On the Refractive Index of Water at Temperatures between 0° and 10°," 'Roy. Soc. Proc.,' vol. 58, p. 228.

at the same temperature. In order that the prism might be in contact with the water-jacket it was necessary that this should be carried by the table of the goniometer, and therefore that it should be as small and light as possible.

A slow stream of water from a tap was allowed to flow through a coil of about 5 metres of "compo" pipe, placed in a metal water-bath supported over a small gas flame; the temperature of the water being kept constant by means of a Harcourt gas regulator. From the coil the water passed through a rubber tube to the water-jacket. This consisted of two flat brass boxes 1.5 cm. deep and 12 cm. in diameter, between which the prism was placed; the lower box being circular, the upper annular. The boxes were fixed together concentrically and their interiors connected by two vertical brass tubes 5.2 cm. long. The brass plate which formed the top of the lower box was 5 mm. thick and 15 cm. in diameter; the levelling screws, by which the water-jacket was supported on the table of the goniometer, worked in holes drilled in the overhanging edge of the plate, and the prism rested on it.

A brass ring with a screw cut on its inner surface was fixed round the top of the central opening in the upper box, a brass tube 2.5 cm. in internal diameter, with a screw cut on its outer surface, worked into the thread on the ring, and by screwing this tube down on to the top of the prism, the prism could be held in position. The object of this particular arrangement was to enable the prism to be filled and emptied by means of a pipette, without interfering with its position, and to allow a thermometer, and a platinum stirring wire, to be introduced into the liquid whose refractive index was to be observed.

The third face of the prism was in actual contact with the flat surface of one of the vertical tubes, by means of which the two boxes were connected together. The cross section of these two tubes was such, that the prism was, as far as possible, surrounded by the water-jacket. Paper tubes, fitted over the ends of the collimator and telescope, projected into the openings in the water-jacket. By packing the spaces between these paper tubes and the water-jacket with cotton wool, the sides of the prism were, to a considerable extent, shielded from air currents, without preventing the adjustment of the prism and telescopes.

Two small metal pipes were fixed to the top of the upper cylindrical box, the one ending just within the box, the other reaching down through one of the connecting tubes already mentioned, nearly to the bottom of the lower box. To these metal pipes rubber tubes were attached; through the one the water from the coil flowed into the jacket, through the other from the jacket to the waste.

By keeping the temperature of the water-bath at about 20° (the temperature necessary varied with the temperature of the room, an

underground one), the temperature of the liquid in the prism could be easily kept within one or two tenths of a degree of 18°.

The liquid in the prism was kept stirred by means of the platinum wire, the end of which was bent round into a ring, and the bulb of the thermometer was immersed in the liquid.

The observations were made with sodium light only, as it had been previously found that, owing to the brilliancy and constancy of the sodium light, it was not only far easier to make observations with it, but that those observations would be more accurate than observations made with light of other refrangibilities.

The readings were made by moving the telescope first from left to right, then from right to left, until the intersection of the cross wires coincided with the image of the sodium line; and the micrometer was read in the same way. After four readings of the micrometer had been made, the prism was reversed by rotating the table of the goniometer, and adjusted for minimum deviation: four readings made, and then the prism again adjusted for minimum deviation, and four more readings made; the prism replaced in its original position, adjusted, and the same number of readings made.

The liquid in the prism was well stirred, and the thermometer read before each adjustment of the prism for minimum deviation. Half the difference between the two sets of eight readings was, of course, the deviation. The readings were made thus in order, as far as possible, to eliminate errors due to the position of the prism, and to slight changes in temperature.

For each solution observations were made with the prism at the temperature of the room, and at 18°. In the former case one set only, as the temperature of the prism did not remain constant, and indeed had usually risen slightly before the one set of readings could be made; in the latter case four sets were made.

The densities of the solutions were determined by means of Dr. Perkins' modification of the Sprengel density tube.* Two of these tubes were used, containing respectively 34·0376 c.c. and 25·1587 c.c. After being filled, the tubes were placed in a water bath at 18° for 20 minutes, the volumes adjusted, and weighed against counterpoises made of the same kind of glass, and having about the same surface areas; the tubes and their counterpoises were wiped carefully with a dry cloth before each weighing, to ensure that, as far as possible, the surfaces were in the same condition as regards moisture. After being weighed, a few more drops of the solutions were introduced into the tubes, which were then replaced in the bath; four determinations being made with each solution.

The water-bath contained a Harcourt gas regulator, and a slow stream of water from the main was run into it; without this the temperature could not be kept down to 18°, the loss of heat by radiation not being sufficient.

The bath was kept stirred by bubbles of air which escaped from an inverted thistle-funnel connected by a rubber tube with a large Woulfe's bottle. A stream of water ran continuously into the bottle, and drove the air out through the rubber tube and thistle funnel. When nearly full of water, the bottle was emptied by a syphon; thus, by the combined action of a continuous stream of water tending to fill the bottle, and the intermittent action of the syphon which emptied it, the water-bath was kept stirred.

The normal and semi-normal solutions were prepared by first making up solutions which contained a gram-molecule in about 800 c.c. or 900 c.c., then determining the strength of these solutions, running the volume required from a burette into a measuring flask, and making the solution up to a known bulk. Distilled water, which had been freed from air by being boiled and allowed to cool under reduced pressure, was used.

The hydrochloric acid was prepared by redistilling the acid sold as "pure redistilled."

The potassium and sodium chloride solutions were prepared from salts sold as "pure recrystallised" (solutions A), and also (solutions B) from salts guaranteed as pure by E. Merck ("für analytische Zwecke"). The "pure recrystallised" potassium chloride contained a good deal of sodium, whilst that obtained from Merck contained hardly any.

The lithium and rubidium chlorides were also purchased from E. Merck, but were of ordinary commercial purity.

The results obtained are given in Table I.

Table I.
Hydrogen Chloride.

Normal solution. 36.78 grams = 1.0091 gram-molecule in 1000 c.c.		Semi-normal solution. 18·24 grams = 0·5005 gram-molecule in 1000 c.c.			
Temp.	Ref. index.	index. Density.		Ref. index.	Density.
15·0°	1:341748		16·4°	1 :337501	
18 ·0°	1 · 341504 1 · 341506 1 · 341514 1 · 341520 1 · 341528	1 · 01646 1 · 01647 1 · 01647 1 · 61647	18·0°	1 ·337360 1 ·337364 1 ·337376 1 ·337382	1 ·00748 1 ·00753 1 ·00757 1 ·00762
Mean	1 ·341514	1 .01647	-	1 •337370	1 .00755

Table I—continued.
Lithium Chloride.

Normal solution. 42 ·40 grams = 0 ·9982 gram-molecule in 1000 c.c.			21 ·161 g	Semi-normal sol grams = 0.4981 grams in 1000 c.c	gram-molecule	
Temp.	Ref. index.	Density.	Temp. Ref. index. Densit			
15 ·0°	1 342142	manual ma	14 ·24°	1 337893		
18 ·0°	1 ·341921 1 ·341922 1 · 341950 1 · 341964	1·02273 1·02274 1·02277 1·02279	18·0°	1 ·337591 1 ·337593 1 ·337593	1 01066 1 01081 1 01091 1 01101	
Mean	1 •341939	1 .02276		1 ·337592	1 .01085	

Sodium Chloride.

Normal solution A. 58·16 grams = 0·9940 gram-molecule in 1000 c.c.			Semi-normal solution A. 29 ·29 grams = 0 ·5006 gram-molecule in 1000 c.c.			
Temp.	Ref. index.	Density.	Temp.	Ref. index.	Density.	
15·8°	1 ·343317		15·6°	1 ·338420		
18 ·0°	1 ·343090 1 ·343095 1 ·343097 1 ·343101	1 ·03916 1 ·03919 1 ·03927 1 ·03928	18·0°	1 :338198 1 :338200 1 :338200 1 :338203	1·01926 1·01927 1·01927 1·01932	
Mean	1 ·343096	1 .03922		1 ·338200	1 .01928	
Normal solution B. 58 39 grams = 0 9980 gram-molecule in 1000 c.c.			emi-normal solu rams = 0 ·4991 g in 1000 c.c	gram-molecule		
15 ·1°	1 · 343329 —		15 · 5°	1 ·338524		
18 ·0°	1 ·343035 1 ·343063 1 ·343066 1 ·343075	1·03916 1·03919 1·03928 1·03933	18 ·0°	1 ·338193 1 ·338196 1 ·338202 1 ·338207	1·01913 1·01916 1·01916 1·01926	
Mean	1 ·343060	1 .03924		1 ·338199	1 01918	

Table I—continued.
Potassium Chloride.

Normal solution A. 74-20 grams = 0.9949 gram-molecule in 1000 c.c.			Semi-normal solution A. 37:13 grams = 0:4979 gram-molecule in 1000 c.c.			
Temp.	p. Ref. index. Density.		Temp.	Ref. index. Density.		
14·0°	1:343380		14·4°	1 :338460		
18·0°	1·342926 1·342926 1·342955	1 ·04482 1 ·04483 1 · 04485 1 · 04496	18.00	1 ·338135 1 ·338147 1 ·338147 1 ·338153	1 ·02204 1 ·02205 1 ·02207 1 ·02208	
Mean	1 · 342936	1 .04487		1 ·338145	1 .02206	
Normal solution B. 74.65 grams = 1.0008 gram-molecule in 1000 c.c.			Semi-normal solu rams = 0.5004 g in 1000 c.c	ram-molecule		
15 ·75°	1 ·343135	343135 —		1:338403		
18·0°	1 ·342905 1 ·342926 1 ·342934 1 ·342934	1 ·04495 1 ·04503 1 ·04503 1 ·04504	18.00	1 ·338139 1 ·338145 1 ·338146 1 ·338167	1 ·02211 1 ·02212 1 ·02217 1 ·02220	
Mean	1 ·342925	1 .04501		1 ·338149	1 .02215	

Rubidium Chloride.

Normal solution. 120'70 grams = 0'9984 gram-molecule in 1000 c.c.				Semi-normal solutions = 0.4991 g in 1000 c.c.	ram-molecule
Temp.	Ref. index.	Density.	Temp.	Ref. index.	Density.
17 ·2°	1:343958		17·4°	1 ·338634	
18 ·0°	1 · 343840 1 · 343882 1 · 343882 — 1 · 343868	1 ·08587 1 ·08599 1 ·08604 1 ·08621 1 ·08603	18:0°	1 · 338577 1 · 338578 1 · 338580 1 · 338601 1 · 338584	1 ·04253 1 ·04255 1 ·04258 1 ·04261 1 ·04257

The probable errors of the determinations were calculated by the ordinary formula $0.674 \sqrt{\frac{\Sigma d^2}{n(n-1)}}$; the mean probable error for the

refractive indices was found to be 4 in the sixth place, and for the densities 2 in the fifth place.

The sensitiveness to change of temperature (i.e., the decrease in the value of the index for an increase of 1°) as calculated from the values given in the table is nearly the same for both the normal and seminormal solutions, the mean value being 0.000095. The value for water as calculated from the values for the indices at 15° and 20°, given by eight different observers, being 0.000080.*

The solutions not being accurately normal or semi-normal, the values for the refractive indices and densities of normal and semi-normal solutions at 18° were calculated from the observed values given in Table I, on the assumption that the differences between the indices and densities of the solutions and those of water are, over this small range, proportional to the weights of salt present in the unit volumes. The values so obtained are given in Table II, those for the potassium and sodium chlorides being the mean values for solutions A and B.

Normal solutions. Semi-normal solutions. Ref. index. Density. Ref. index. Density. Hydrogen chloride 1:341438 1 .01631 1 :337366 1.00754 Lithium chloride 1.01089 1.3419551.022801 .337608 Sodium chloride 1 .338201 1:01923 1:343113 1.03940 Potassium chloride 1 .342955 1:04505 1 .338155 1.02214Rubidium chloride 1.3438821.08616 1:338593 1.04264

Table II.

Table II shows that both the densities and the refractive indices as a rule increase with the molecular weight, but that in the latter case there is one remarkable exception. The refractive index of potassium chloride is slightly lower than that of sodium chloride.

This fact has already been noticed by Bender† and Borgesius.‡ Bender's observations were made by the hollow prism method, with solutions containing from 0.5 to 4.5 gram-molecules in the litre, and at temperatures between 16° and 21°; he states (p. 92) that the solutions of potassium and sodium chloride had nearly identical refractive indices, those of the latter being slightly the greater, especially with the more concentrated solutions.

Borgesius's observations were made by an interference method, and

^{*} Conf. Dufet, 'Recueil de Données Numériques,' p. 87.

^{† &#}x27;Wied. Ann.,' vol. 39, p. 88.

^{‡ &#}x27;Wied. Ann.,' vol. 54, p. 221.

he gives his results as the differences between the indices of his solutions and that of water; his Table I* shows that the values for the potassium chloride solutions were always lower than those for the corresponding sodium chloride solutions.

The refractive index of the solution of a salt clearly depends on the influence both of the solvent and of the salt in solution. In order that the values obtained with different salts should be comparable, it is necessary that the solutions should be similar, *i.e.*, that in unit volume there should be the same weight of solvent and of salt, or the same weight of solvent and weights of salt bearing the same relation to the molecular weights of the salts.

Such is seldom, if ever, the case with aqueous solutions at least. A litre of a normal solution contains, together with the gram-molecular weight of the salt, a weight of water which is different for different salts.

Hence the refractive indices of the solutions of any two salts cannot be taken as a measure of the influence which the several salts exert on the velocity of light, unless it has been shown that the unit volumes of the solutions contain equal weights of water, together with either equal weights of the salts, or weights which bear the same ratio to the molecular weights.

Table III gives the weight in grams of the water contained in 1000 c.c. of the solutions whose refractive indices and densities are given in Table II, obtained by subtracting from the weight of 1000 c.c. of the solution the weight of salt contained in that volume.

	Normal solution.	Semi-normal solution.
Water	998 •666	
Hydrogen chloride	979.850	989 316
Lithium chloride	$980 \cdot 316$	989.653
Sodium chloride	980.885	989 .980
Potassium chloride	9 7 0 · 463	984 ·851
Rubidium chloride	$965 \cdot 272$	982 -199

Table III.

The table shows that in equal volumes of the solutions of the chlorides of hydrogen, lithium, and sodium nearly equal weights of water are present, but that such is not the case with the solutions of the two other chlorides.

In a litre of a normal solution of potassium chloride there are about 10 grams, and in a semi-normal solution about 5 grams less water than

in the corresponding solutions of sodium chloride; hence if the chlorides of the two metals had, when present in solution in molecular proportions, equal powers of retarding the velocity of light, the solution of the potassium salt might be expected to have a lower refractive index than that of the sodium salt, as the unit volume contains, in addition to the salt, less water.

At present we are not in a position to distinguish between the retardation due to the substance in solution and that due to the solvent. If, as a first attempt, we assume (which is, of course, improbable) that the presence of the salt merely causes the water to occupy a greater volume without altering any of its properties other than those which depend on its density, we can calculate approximately the refractive index of the water in the solution.

When two gases are mixed and no mutual action is known to occur, we regard each gas as unchanged except that its density is reduced by the admixture. If a mixture of liquids or the solution of a salt, where no mutual action is known to occur, be similarly regarded, we may consider each of the liquids or the solvent as changed only in respect of its density. If again we attribute the change of refractive index with temperature solely to the change in the density of the liquid, we may make the hypothesis that the effect on the refractive index of water of a change of density is the same when it is expanded by admixture and when it is expanded by rise of temperature. No doubt such a hypothesis, resting upon two hypotheses each of which is improbable, has itself a very small probability, but I have thought it worth while to reckon what the refractive indices of the water in the various solutions would be on this hypothesis. The difference between this value and the observed value of the index of the solution furnishes more probable value for the influence which the salt may be supposed to exert on the velocity of light than that obtained by subtracting the index of water from the index of the solution at the same temperature.

From Landolt and Börnstein's tables the temperatures were ascertained at which water has the same density as that contained in the various solutions, and then from the same tables the refractive index of water for these temperatures and densities.

The values for the differences between the observed indices of the various solutions and the index of water at 18° are given in the second and third columns of Table IV, and the differences between the observed indices and the values for the indices of water, calculated on the above assumption, in the fourth and fifth columns.

The table shows that the differences between the refractive indices of the solutions, and that of water at 18° increase with the molecular weights of the salts in solution, except in the case of potassium chloride, but if the differences are calculated on the assumption that the refractive index of the water in the solutions is less than that of

Normal Semi-normal Normal Semi-normal solution. solution. solution. solution. 0.00423 0.00792 Hydrogen chloride... 0.00831 0:01551 Lithium chloride ... 0.00882 0.00448 0.01583 0.00804 Sodium chloride 0.00998 0.00507 0.016790.008540.01036 Potassium chloride... 0.00982 0.00502 0.02047Rubidium chloride ... 0.00546 0.02328 0.01172 0.01075

Table IV.

water in its ordinary condition, then potassium chloride no longer forms an exception, and the differences increase with the molecular weights of the salts; the increase, however, does not bear any apparent relation to the increase in the molecular weights.

The differences for the normal solutions, calculated in both ways, are slightly less than double those for the semi-normal.

The object of these experiments was the determination of the refractive indices and densities of normal and semi-normal aqueous solutions of hydrogen chloride and the chlorides of the alkalis at a uniform temperature; the results obtained at 18° are set forth in Table I, the indices being given to six places of decimals and the densities to five places.

In Table II the results corrected for small errors in the strengths of the solutions are given. The table shows that both the densities and the refractive indices increase with the molecular weight of the substance in solution, except in the case of the refractive index of potassium chloride, which is slightly lower than that of sodium chloride.

Table III gives the weight of water contained in 1000 c.c. of each of the solutions, and Table IV the differences between the refractive indices of the solutions, and the refractive index of water under ordinary conditions, and also the differences between the refractive indices of the solutions and the calculated indices of the water contained in the solutions.

[Note.—From the data given in Table I, it is not possible to draw any satisfactory conclusions as to the sensitiveness of the different solutions. The values for the indices at temperatures other than 18°, rest on single sets of observations, and in some cases there was not sufficient difference between the temperature at which these observations were made and 18°, to enable the rate of change of the index to be determined at all accurately.

I have, therefore, made some further observations with the same solutions of hydrogen chloride and the chlorides of lithium, sodium,

and potassium, and also with water. In both the rubidium solutions a mould had developed, and therefore no observations were made with these two solutions.

The observations were made in the same way as those already described, except that (1) the gas regulator was removed from the water bath containing the coil, and the temperature was allowed to rise, and (2) all the measurements were made with the prism in one position.

The temperature of the prism rose slowly, about 2° in an hour; the prism was not reversed in order to avoid exposing its surfaces to the cooling action of the air of the room. The object of the experiments being to ascertain the relative values of the index of a solution at different temperatures, and not the absolute value at any particular temperature, the result would not be affected by any small error due to the observations having been made with the prism in one position of minimum deviation and in one position only.

The values obtained were plotted, one unit in the fifth place being represented by 1 mm., and the rate of change, the "sensitiveness," ascertained from the plotting.

The results are given in the table: in the second and fifth columns the temperatures between which the observations were made, in the third and sixth the number of observations, and in the fourth and seventh the decrease of the index for an increase of 1°.

Water 11 ·10°—20 ·85° 6 0 ·000078 Hydrogen chloride 10 ·85 —18 ·40 7 0 ·000077 10 ·05°—17 ·45° 7 0 ·000072 Lithium chloride 12 ·10 —21 ·20 8 0 ·000083 9 ·75 —18 ·65 6 0 ·000073 Sodium chloride, B. 12 ·25 —21 ·10 13 0 ·000109 10 ·00 —19 ·5 6 0 ·000087	THE SECRETARY SHARE THE SE	Normal solution.			Semi-normal solution.		
	Hydrogen chloride Lithium chloride Sodium	10 ·85 —18 · 40 12 ·10 —21 ·20	7 8	0 ·000077 0 ·000083	9 ·75 —18 ·65 10 ·00 —19 ·5	6	0 .000073

The table shows that between 10° and 20° the "sensitiveness" of the normal solutions is greater than that of the semi-normal solutions; and further, that it increases with the increase of the refractive index of the solution.

The value for water between 10° and 20° calculated from the values given by Dufet* is 0.000071, or slightly less than that obtained in these experiments.—December 31, 1898.]